

Experimentally determined solubilities of Pt in a haplobasaltic melt under well constraint conditions of f_{O_2} , P, T, and H_2O activity

W. Ertel
M. Pichavant
B. Scaillet

CNRS-CRSCM, 1A Rue de la Fèrolierie, 45071 Orléans Cedex 2,
France

Experimental investigations of the solubility behaviour of highly siderophile elements (e.g. Pt, Rh, Ir, Re) in a melt of An-Di eutectic composition at 1 atm total pressure have determined metal/silicate partition coefficients of several orders of magnitude difference to naturally observed values. These results are decisive in the development of theories concerning the formation of the Earth and the explanation of the yet unsolved 'overabundance' problem of highly siderophile elements (HSE) in the Earth's upper mantle.

In respect to reconcile experimental and naturally observed metal/silicate partition coefficients higher pressures and the influence of H_2O on the solubility behaviour of HSE are the most likely candidates under discussion.

Performing piston cylinder and multi anvil experiments, high pressure metal/silicate partition coefficients can be determined, however, the f_{O_2} is not well constraint in these type of experiments. Additionally for some elements the applied f_{O_2} seems to have a more important influence on the partition coefficient, and pressure plays only a minor role.

Internally heated pressure vessels cover a pressure range up to 10 kbars, and temperatures up to 1400°C with H_2 /Argon gas mixtures as pressure medium. With this technique experiments can be performed at elevated pressures and temperatures both under well constraint f_{O_2} and H_2O activity conditions. The f_{O_2} can be measured using f_{O_2} sensor assemblies like Pt/Ni/NiO or Pt/Co/CoO. The concentrations of H_2O in the melts can be determined by Karl-Fischer titration and recalculated to water activities applying the Burnham's model.

Experimental

The solubilities of Pt in a silicate melt of An-Di eutectic starting composition were experimentally determined applying internally heated pressure vessels equipped with an outer Kanthal resistance, an inner Pt resistance to reach temperatures up to

1400°C, and an improved rapid quench device. The temperature was continuously measured by 3 type-B Pt/Rh thermocouples situated beside the upper and lower end of the samples, and one exactly in the middle of both. The temperature control was performed by the middle thermocouple. The temperature control was better than $1300^\circ\text{C} \pm 0.5^\circ\text{C}$ in all experiments. The temperature gradient over the sample length of 2.2 cm was less than 10°C .

The used capsule material consisted of pure Pt (od: 2.9; id: 2.5 mm), which served at the same time as Pt source. The starting melt composition was prepared according to a gelling procedure. To attain a high homogeneity of the starting glass material the gel was twice fused and reground. 700 mg of finely ground starting glass was filled into a capsule, H_2O was added, and the capsule was sealed by welding. Weight loss was checked while preparation of the capsules, and directly before and after the experiment. Capsules with weight loss were immediately discharged. Experiments consisted of up to 6 capsules with different amount of water added to the charge (from 0 to 6 at 2 kbar; 0 to 10 wt.% H_2O added for 4 kbar runs).

The experimental run duration was 12 h, after proofing in a time series (3 runs with 6, 12, and 24 h) that equilibrium solubilities could be attained in this period.

Analytical

The bulk composition of the run products were determined by electron microprobe techniques. The prepared samples were then used directly in laser ablation ICP-MS measurements for the determination of the Pt concentration in the glass. Calibration of the ICP-MS was performed applying Pt glass standards of identical glass composition in comparison with the samples. The H_2O concentration was determined using Karl-Fischer titration techniques, and recalculated for H_2O activities using the Burnham model.

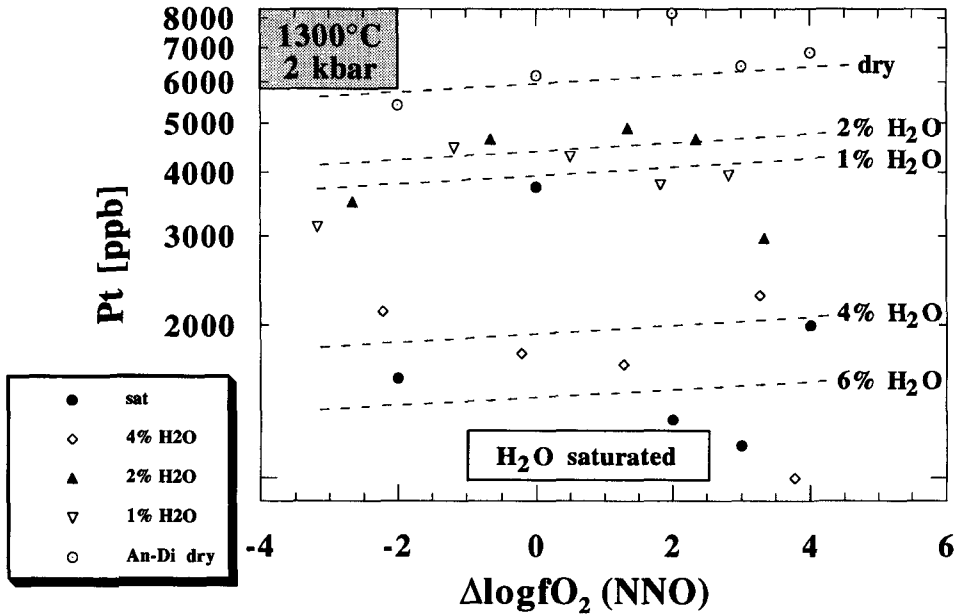


FIG. 1. Experimental results of runs at 2 kbar and 1300°C.

Results

The results of the LA-ICP-MS measurements for the 1300°C and 2 kbar runs are given in Fig. 1, and show an absolute solubility range between 1 and 10 ppm in all experiments. All runs show a decrease of the Pt solubility with increasing amount of water present in the melts. The range in solubility at constant f_{O_2} (e.g. NNO + 2) decreases from around 8 ppm for the dry pure An-Di eutectic system to less than 1.3 ppm for the water saturated system (6 wt.% H₂O at 2 kbar).

At constant H₂O content in the samples the solubility of Pt increases only slightly with increasing f_{O_2} .

Discussion

Based on the present results an increasing amount of H₂O leads to a decrease of the solubility of Pt in the silicate melt at constant conditions of f_{O_2} , pressure and temperature. In comparison to the dry system of

An-Di the absolute solubility of Pt (8 ppm) is reduced to about 1 ppm in the H₂O saturated system - a drop in solubility of less than one order of magnitude.

Metal/silicate partition coefficients can be calculated from these solubility data. For the dry pure An-Di system at 1300°C and IW-1 the $D^{M/S}$ is 4.6×10^8 . The value for the H₂O saturated systems is 2.2×10^9 , so even higher than the dry system. Water therefore has not the expected influence to lower the gap between experimental and naturally observed metal/silicate partition coefficients. Pressure, however, seems to help to decrease the discrepancy between 1 atm metal/silicate partition coefficient of Pt and the naturally values: The $D^{M/S}$ of Pt at 1 atm is 3.2×10^9 , while the 2 kbar value for the same f_{O_2} conditions is 4.6×10^8 . An increase of pressure therefore decreases the ratio of the experimental to natural observed partition coefficients. Experiments at higher pressures under well constraint conditions of f_{O_2} , temperature, composition and water activity is necessary to confirm this observation.